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# Hybrid Supermolecule-Polarizable Continuum Approach to Solvation: Application to the Mechanism of the Stevens Rearrangement\*

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## ABSTRACT

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Semiempirical molecular orbital theory has been used to study the effects of solvation by acetonitrile on the Stevens rearrangement of methylammonium formylmethyllide to 2-aminopropanal. Three methods of solvation have been used to investigate both the electrostatic and specific solvent-solute effects of solvation: a supermolecule calculation involving the complete geometry optimization of up to six solvent molecules about the solute, the conductor-like screening model (COSMO) polarizable continuum method which allows for geometry optimization of the solute in a solvent defined by its dielectric constant, and a hybrid method in which up to five solvent molecules are incorporated inside the solute cavity and complete geometry optimization of the complex is carried out within the polarizable continuum. A comparison of the calculated geometries, rearrangement activation energies, and enthalpies of solvation from these approaches is presented, and the explicit versus bulk solvation effects are discussed. The overall effect of all methods for incorporating solvation effects is that the radical pair pathway is preferred over the concerted mechanism. © 1996 by John Wiley & Sons, Inc.

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## Introduction

The incorporation of solvent effects in quantum chemical calculations has been a popular area of development for the past few years, with developments in the all atom,<sup>1</sup> simplified solvent,<sup>2</sup> and polarizable continuum<sup>3</sup> approaches to solvation. There are a number of polarizable continuum methods available for calculation of solvation energy, such as the self-consistent reaction field (SCRF) method of Rivail,<sup>4</sup> and the conductor-like screening model (COSMO) of Klamt and Schüürmann<sup>5</sup>; however, these all suffer from the fundamental problem of ignoring specific solvent-solute interactions.

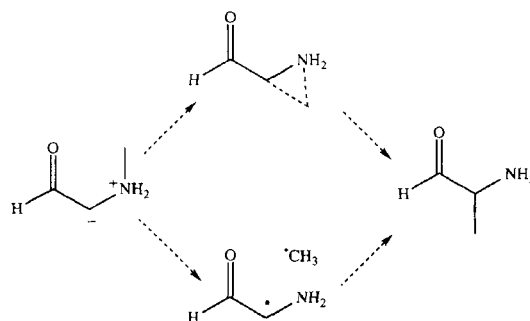
For the problem of a solute with a small dipole in a solvent with a relatively low dielectric constant, the specific solvent-solute interactions may be the largest contributions to the solvation energy.<sup>6</sup> In this case, it has been suggested that a molecular dynamics approach would be most appropriate. The question then arises—How can we know which approach is appropriate, and is there a way of incorporating both electric field and specific solvent-solute effects in a quantum chemical calculation? In this study, we investigate the possible solution of describing individual solvent molecules in the molecular wave function, treating the remainder of the solvent as a bulk dielectric and optimizing the energy of the supermolecule within the polarizable continuum.

Studying solvation by the supermolecule approach alone is only possible for a few solvent molecules<sup>7–9</sup> and it is certainly not feasible to include enough solvent molecules to obtain a complete description of solvation. A supermolecule approach with a solvent molecule embedded in the cavity along with the solute molecule has been touched upon by Szafran and coworkers.<sup>10</sup> This study, on the tautomerization of pyridones, found that the inclusion of one hydroxide ion in the cavity provided better correlation with experimental results than the polarizable continuum alone. Karelson and Zerner<sup>11</sup> incorporated two water molecules within a PCM in their studies of solvation of nitrogen-containing heterocycles, and noted that spectroscopic shifts calculated using this method were in better agreement than a continuum alone. Recent work on metal ion solvation by Furuki and co-workers<sup>12</sup> included several water

molecules inside the cavity and obtained close correlation with experimental results; however, neither of these studies optimized the geometry of the complex within the cavity.

In this study, the specific solvent-solute effects of acetonitrile (the preferred organic solvent) on the Stevens rearrangement of methylammonium formylmethylide (Scheme 1) will be investigated by optimizing the positions of up to six solvent molecules around the solute. The geometry optimizations are done using the semiempirical PM3 Hamiltonian,<sup>13</sup> which has been seen to give results comparable to high-level *ab initio* calculations on these systems. COSMO is an attractive method for incorporating solvation in the calculation as energy derivatives are easily obtained and hence geometry optimization within the continuum is possible. It also has a more realistic cavity shape than the sphere (or ellipse) of SCRF. COSMO is used to incorporate solvent effects upon both the individual solute molecules and the solvated clusters.

Our previous gas-phase calculations on the Stevens rearrangement of alkylammonium ylides<sup>14–16</sup> have shown the radical mechanism is favored over the concerted mechanism by roughly 80 kJ mol<sup>-1</sup>; however, the highly stereoselective nature of the rearrangement indicates that there could be a concerted process in action. Our previous SCRF calculations<sup>17</sup> show that there is little electrostatic solvent effect on this rearrangement. Relative energies obtained from the calculations in this study should give an indication of the importance of the solvent on the relative energies of the concerted and dissociative pathways of the Stevens rearrangement.



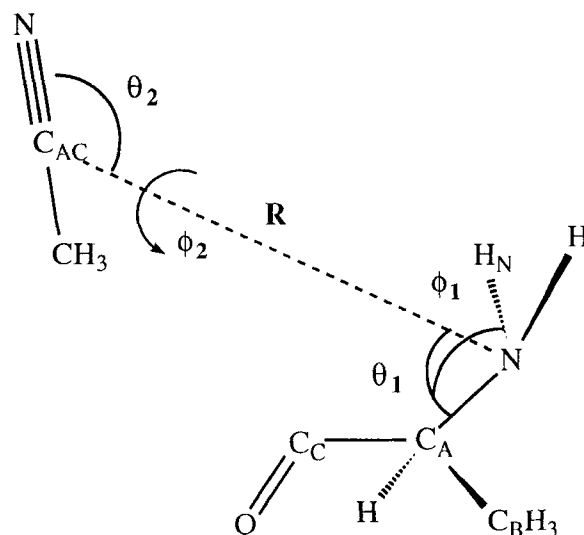
**SCHEME 1.** The Stevens rearrangement of methylammonium formylmethylide, showing both the concerted and radical pair pathways.

## Methods

Standard semiempirical calculations have been carried out using the MOPAC 93<sup>18</sup> program. All geometries have been optimized with the PRECISE keyword and, where possible, using the eigenvector-following algorithm of Baker.<sup>19</sup> In the COSMO calculations, each atom was broken up into 32 segments, producing up to 800 individual segments per molecule for the larger systems. The van der Waals radii were taken from defaults, which were calculated at PM3. COSMO calculations on the uncomplexed species showed that the optimum energy was obtained with an RSolv value of 1.0.

Supermolecule optimizations were done in two stages. First, the positions of the acetonitrile molecules were optimized with the parameters describing the solute molecule held constant. All molecular parameters were then freed for a complete geometry optimization. The concerted transition structure was characterized by geometry optimization toward the starting ylide and product amine along the reaction coordinate. The acetonitrile molecules in this case were described by five parameters, shown in Figure 1: the distance  $R$  from the solute nitrogen to the central carbon of the acetonitrile ( $C_{AC}$ ); the angle  $\theta_1$  between  $N-C_{AC}$  and  $N-C_A$ ; the torsional angle  $\phi_1$  between  $N-C_{AC}$  and  $C_A-H_N$  where  $H_N$  is one of the hydrogen atoms on the amine group ( $R$ ,  $\theta_1$ , and  $\phi_1$  are, in effect, polar coordinates of  $C_{AC}$  relative to  $N$ ); the angle  $\theta_2$  between the solute nitrogen, the  $C_{AC}$ , and the acetonitrile nitrogen (hence,  $0 < \theta_2 < 90$  indicates the nitrogen end of the acetonitrile is oriented toward the solute,  $90 < \theta_2 < 180$  indicates it is oriented away from the solute); and the torsional angle  $\phi_2$  between the  $N-C$  of the acetonitrile and  $N-C_A$ , which gives an indication of the conical movement of the solvent molecule.

Geometries of the solute complexed to varying numbers of acetonitrile molecules are given in Table I, and their complexation energies in Figure 3. Geometries of the solute and complexes optimized with COSMO are also given in Table I, and their complexation energies in Figure 4. Positions of the acetonitrile molecules about these solute molecules optimized at both PM3 and COSMO are available as Supplementary Material; the structures of the largest optimized COSMO cluster for



**FIGURE 1.** The five parameters used to describe solvent position.

each species are given in Figure 2. Relative energies of the models of solvation considered in this article are presented in Table II, and as a function of number of acetonitrile molecules in Figure 5.

## Results and Discussion

### GEOMETRIES OF SPECIES

In a previous study, we presented the geometries for the species involved in the gas-phase Stevens rearrangement of methylammonium formylmethylide.<sup>14</sup> In the first stage of the current study, we have surrounded the gas-phase species of this rearrangement with varying numbers of acetonitrile molecules and performed complete geometry optimization of the resulting supermolecules. By and large, the geometries of the reacting species have changed very little from our previous study, as seen in Table I. The bond distances and angles of all species in general show little variation with the number of complexing acetonitrile molecules, apart from the two dihedral angles,  $OC_C C_A N$  and  $OC_C C_A C_B$ , describing the orientation of the carbonyl group on the amine (rotation about the  $C_C C_A$  bond). It is worth noting that a parameter one might expect to change noticeably, the  $C_A N C_B$  angle (in effect, the reaction coordinate) of the concerted transition structure, remains unaltered with the addition of several coordinating acetonitrile molecules.

**TABLE Ia.**  
**Geometries of Amine With Varying Number of Acetonitrile Molecules ( $\epsilon = 1$ ,  $\epsilon = 35.9$ ).<sup>a</sup>**

	0 <sup>b</sup>	1	2	3	4	5	6
C <sub>A</sub> N <sup>c</sup>	1.484 (1.489)	1.484 (1.489)	1.484 (1.489)	1.483 (1.486)	1.484 (1.486)	1.485 (1.486)	1.483
C <sub>C</sub> C <sub>A</sub>	1.528 (1.525)	1.529 (1.527)	1.528 (1.523)	1.527 (1.519)	1.528 (1.516)	1.526 (1.516)	1.524
OC <sub>C</sub>	1.207 (1.217)	1.209 (1.217)	1.209 (1.215)	1.208 (1.216)	1.209 (1.217)	1.210 (1.216)	1.208
C <sub>B</sub> C <sub>A</sub>	1.522 (1.522)	1.522 (1.522)	1.522 (1.522)	1.523 (1.524)	1.523 (1.525)	1.522 (1.525)	1.524
C <sub>C</sub> C <sub>A</sub> N	107.5 (107.7)	107.5 (108.0)	107.5 (110.9)	109.1 (112.8)	108.4 (113.2)	108.3 (113.3)	112.6
OC <sub>C</sub> C <sub>A</sub>	123.4 (123.0)	123.2 (122.6)	123.4 (123.6)	123.5 (124.1)	123.1 (124.0)	122.8 (124.2)	124.1
C <sub>C</sub> C <sub>A</sub> C <sub>B</sub>	112.1 (112.3)	111.9 (112.2)	112.0 (109.0)	110.3 (108.4)	110.8 (108.8)	112.6 (108.9)	108.4
OC <sub>C</sub> C <sub>A</sub> N	274.4 (274.8)	274.5 (276.3)	274.2 (319.2)	294.1 (338.5)	289.3 (2.7)	200.6 (6.6)	330.4
OC <sub>C</sub> C <sub>A</sub> C <sub>B</sub>	40.5 (40.4)	40.5 (42.5)	40.5 (85.7)	60.7 (105.6)	55.4 (129.6)	327.1 (133.9)	97.8

<sup>a</sup>In all tables, bond distances are in Ångströms, angles in degrees.<sup>b</sup> $\epsilon = 1.0$  parameters from ref. 14.<sup>c</sup>Atom labels are shown in Fig. 1.

In the second stage of this study, we optimized the gas-phase supermolecules within COSMO. This leads to some change in the solute geometry, as seen in Table I. Here two effects are seen, the first being the effect on the geometry of the continuum.

This is small, but significant, the largest geometry changes being in the concerted transition geometry and the aminoformyl methyl radical. These changes can be rationalized in the sense of the large charge separation seen in the radical, and the relaxation of

**TABLE Ib.**  
**Geometries of Ylide With Varying Number of Acetonitrile Molecules ( $\epsilon = 1$ ,  $\epsilon = 35.9$ ).**

	0 <sup>a</sup>	1	2	3	4	5	6
C <sub>B</sub> N	1.516 (1.502)	1.513 (1.503)	1.513 (1.504)	1.511 (1.503)	1.512 (1.504)	1.510 (1.504)	1.510
C <sub>A</sub> N	1.409 (1.441)	1.415 (1.443)	1.417 (1.444)	1.421 (1.444)	1.426 (1.442)	1.422 (1.440)	1.424
C <sub>C</sub> C <sub>A</sub>	1.420 (1.386)	1.415 (1.386)	1.413 (1.383)	1.409 (1.387)	1.409 (1.389)	1.410 (1.390)	1.406
OC <sub>C</sub>	1.233 (1.262)	1.236 (1.262)	1.237 (1.265)	1.240 (1.261)	1.239 (1.258)	1.238 (1.258)	1.241
C <sub>A</sub> NC <sub>B</sub>	114.3 (112.3)	113.9 (112.0)	113.6 (112.4)	113.2 (112.1)	113.2 (111.5)	113.8 (113.0)	113.9
C <sub>C</sub> C <sub>A</sub> N	120.8 (123.5)	121.2 (123.6)	121.2 (123.4)	121.8 (123.6)	121.5 (123.1)	121.4 (122.9)	121.7
OC <sub>C</sub> C <sub>A</sub>	123.4 (124.9)	123.8 (125.0)	124.0 (125.0)	124.4 (125.0)	124.4 (124.9)	124.3 (125.1)	124.7
C <sub>C</sub> C <sub>A</sub> NC <sub>B</sub>	96.3 (96.3)	97.8 (98.2)	98.7 (97.4)	110.8 (94.0)	90.1 (99.4)	88.6 (81.1)	86.1
OC <sub>C</sub> C <sub>A</sub> N	359.5 (0.5)	0.2 (2.3)	359.8 (359.3)	359.7 (0.8)	358.3 (0.4)	358.0 (3.2)	356.9

<sup>a</sup> $\epsilon = 1.0$  parameters from ref. 14.

**TABLE 1c.**  
**Concerted TS Geometries With Varying Number of Acetonitrile Molecules ( $\epsilon = 1$ ,  $\epsilon = 35.9$  in Parentheses).**

	0 <sup>a</sup>	1	2	3	4	5	6
C <sub>B</sub> N	1.792 (1.848)	1.794 (1.851)	1.801 (1.845)	1.795 (1.846)	1.797 (1.844)	1.800 (1.840)	1.794
C <sub>A</sub> N	1.474 (1.473)	1.474 (1.473)	1.475 (1.473)	1.476 (1.473)	1.476 (1.473)	1.476 (1.473)	1.475
C <sub>C</sub> C <sub>A</sub>	1.449 (1.425)	1.451 (1.427)	1.445 (1.425)	1.450 (1.426)	1.450 (1.427)	1.449 (1.427)	1.450
OC <sub>C</sub>	1.222 (1.245)	1.221 (1.244)	1.226 (1.243)	1.221 (1.243)	1.220 (1.243)	1.222 (1.242)	1.221
C <sub>A</sub> NC <sub>B</sub>	72.1 (70.2)	71.9 (69.4)	71.5 (70.3)	71.2 (70.2)	71.2 (70.1)	71.2 (70.1)	71.2
C <sub>C</sub> C <sub>A</sub> N	119.9 (122.1)	119.9 (122.1)	120.4 (122.2)	119.9 (122.0)	119.9 (122.0)	119.9 (122.0)	120.0
OC <sub>C</sub> C <sub>A</sub>	124.0 (124.7)	124.0 (124.7)	124.2 (124.9)	124.4 (124.9)	124.7 (124.8)	124.6 (124.8)	124.3
C <sub>C</sub> C <sub>A</sub> NC <sub>B</sub>	108.8 (107.2)	109.0 (107.7)	107.7 (107.8)	107.7 (107.4)	107.8 (107.3)	107.4 (107.3)	107.2
OC <sub>C</sub> C <sub>A</sub> N	355.7 (356.0)	355.2 (355.8)	352.4 (357.5)	353.8 (357.0)	357.1 (358.0)	357.0 (357.7)	354.0

<sup>a</sup> $\epsilon = 1.0$  parameters from ref. 14.

the small heterocycle of the transition state. The second geometry effect is that of the addition of solvent molecules to the continuum. As was seen for the gas-phase cluster, there is little effect on the solute geometry from the incorporation of solvent molecules. In the amine, again, there is variation in the values of OC<sub>C</sub>C<sub>A</sub>N and OC<sub>C</sub>C<sub>A</sub>C<sub>B</sub> due to the facility of rotation about C<sub>C</sub>C<sub>A</sub>.

The geometries reported in this study are for the lowest energy conformation of the cluster, generated by a systematic search for local minima using several positions of solvent molecules as

starting points. Typically, 20 starting geometries were used with acetonitrile molecules occupying different positions about the solute. When optimizations involve several polar solvent molecules, there are two interactions which effect the energy of the system, and hence the optimized geometry: the interaction of the solvent molecule with the solute molecule, and the interaction of the solvent molecule with other solvent molecules. A pictorial representation of each of the largest complexes is given in Figure 2. It can be seen that, when there are a large number of acetonitrile molecules in the

**TABLE 1d.**  
**Amine Radical Geometries With Varying Number of Acetonitrile Molecules ( $\epsilon = 1$ ,  $\epsilon = 35.9$  in Parentheses).**

	0 <sup>a</sup>	1	2	3	4	5
C <sub>A</sub> N	1.373 (1.350)	1.372 (1.352)	1.370 (1.362)	1.369 (1.365)	1.369 (1.370)	1.370
C <sub>C</sub> C <sub>A</sub>	1.456 (1.426)	1.456 (1.426)	1.453 (1.435)	1.450 (1.441)	1.448 (1.449)	1.447
OC <sub>C</sub>	1.205 (1.242)	1.216 (1.240)	1.218 (1.236)	1.218 (1.227)	1.219 (1.218)	1.220
C <sub>A</sub> C <sub>C</sub> N	121.1 (122.3)	121.4 (122.4)	121.6 (122.3)	121.4 (121.1)	121.3 (121.6)	121.3
OC <sub>C</sub> C <sub>A</sub>	122.2 (121.6)	121.8 (122.5)	121.9 (121.7)	122.4 (122.9)	122.8 (122.4)	122.8
OC <sub>C</sub> C <sub>A</sub> N	184.1 (182.1)	184.7 (183.0)	183.6 (183.1)	184.8 (187.5)	184.4 (187.9)	182.4

<sup>a</sup> $\epsilon = 1.0$  parameters from ref. 14.

**TABLE II.**  
Relative Energies (in  $\text{kJ mol}^{-1}$  Relative to Amine) of  
Species at Several Levels of Theory.

	Ylide	Concerted TS	Radical Pairs
PM3 <sup>a</sup>	99	227	325
MP2/6-31G(d) <sup>b</sup>	139	355	420
COSMO PM3	28	203	310
SCRF MP2/6-31G(d) <sup>a</sup>	124	327	410
PM3 (+6 $\text{CH}_3\text{CN}$ )	68	228	316
COSMO PM3 (+5 $\text{CH}_3\text{CN}$ )	50	216	297

<sup>a</sup>From ref. 15.

<sup>b</sup>From ref. 14.

calculation, most of the solvent molecules gather on one "side" of the solvent molecule. The lowest energy conformation thus resembles an appropriate  $n$ -mer coordinated to the solute molecule. Optimizations of the complex in the continuum show considerable changes in the positions of the acetonitrile molecules. This is not surprising, given the weak coordination of the solvent to the solute.

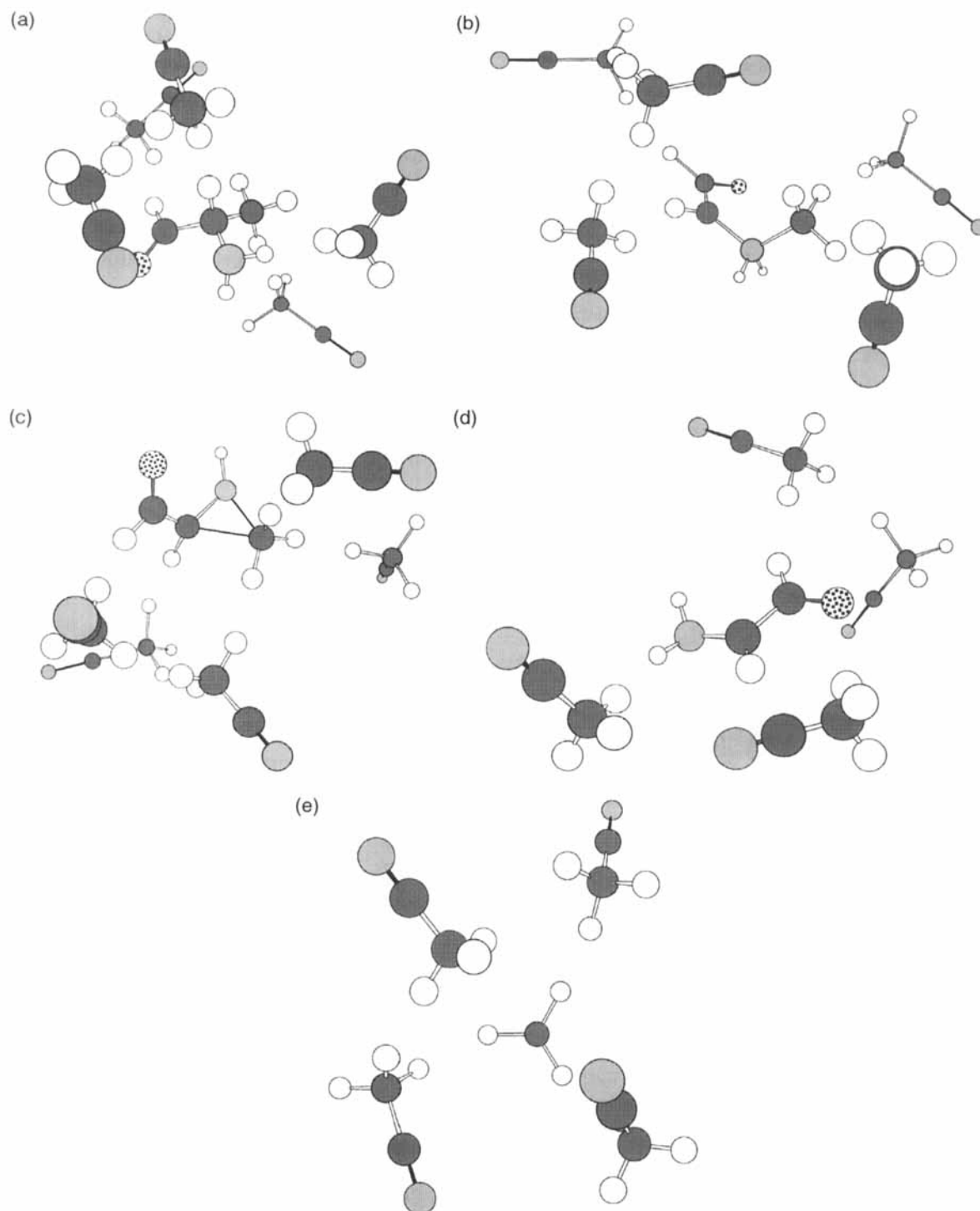
From the optimizations within the continuum, some specific solvent-solute effects are in evidence. In the amine, there are two acetonitrile molecules interacting with the lone pair on the amine nitrogen. These appear at  $\theta_1$  values of around  $130^\circ$  and  $66^\circ$  and are common to the COSMO complexes of three, four, and five solvent molecules. A third acetonitrile molecule common to the two largest clusters is aligned "side-on" to the methyl group at  $\theta_1 = 85^\circ$ . In the ylide, there are two acetonitrile molecules in similar positions in the two largest COSMO clusters, with  $\theta_1$  values of  $55^\circ$  and  $68^\circ$  in the largest solvated ylide. These are above and below the  $\text{N}-\text{C}-\text{C}-\text{O}$  plane, with the methyl end of the solvent molecule oriented toward the plane (and hence, one assumes, a delocalized  $\pi$ -type orbital). Satisfyingly, the concerted transition geometry shows two acetonitrile molecules above and below the  $\text{N}-\text{C}-\text{C}-\text{O}$  plane, as in the ylide ( $\theta_1 = 44^\circ, 48^\circ$ ) and an acetonitrile molecule at  $\theta_1 = 119^\circ$ , which behaves similarly to that near the methyl group in the amine. In the amine radical, there are again acetonitrile molecules above and below the  $\text{N}-\text{C}-\text{C}-\text{O}$  plane ( $\theta_1 = 48^\circ, 61^\circ$ ), as well as a common solvent molecule oriented toward the nitrogen atom at  $\theta_1 = 138^\circ$ . Specific interactions can now be assumed: two solvating acetonitrile molecules co-ordinate to the delocalized orbital in the ylide;

these remain coordinated in the transition geometries, with a third solvent molecule becoming important, coordinating to the migrating methyl group in the concerted transition geometry, or to the amine end of the radical in the dissociative pathway. The delocalization, and hence the interaction of the two solvating acetonitriles, is lost with the formation of the amine, and solvent molecules cluster at the methyl group and at the amine lone pair. Unfortunately, the calculation of the influence on the energy of these specific effects individually is beyond the scope of this study, however, it explains the difference in complexation energies discussed below. It is also worth noting that we have neglected the time scale of reaction, and treated the ideal situation that the solvent is always in equilibrium with the solute. Although this is not likely to be the case, it is done to obtain the maximum solvent effect—presumably energies presented here are an upper bound to the true energy of the individual species.

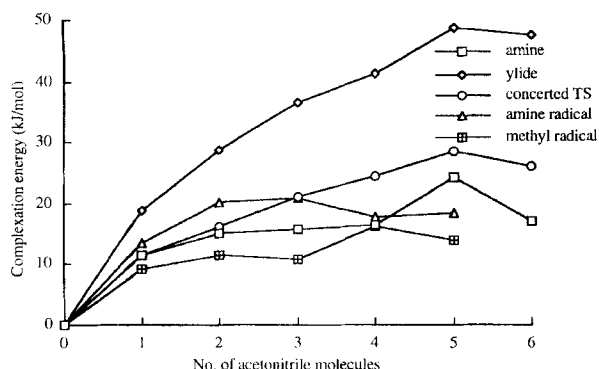
### COMPLEXATION ENERGIES

The complexation energy of the five species as a function of number of coordinating acetonitrile molecules is given in Figure 3. The energies are all relative to the energies of the solute molecule and the appropriate  $n$ -mer of acetonitrile calculated at PM3. The lines indicating the complexation energy start to flatten out at three or four solvent molecules for the radicals and at five or six solvent molecules for the singlet species and hence it is anticipated that the major specific interactions between solvent and solute are adequately covered at these numbers of solvent molecules. The coordination to the ylide is the strongest, which could be expected from the charge separation seen in this molecule. By extrapolating these lines one would expect a specific solvent-solute energy of between 10 and 20  $\text{kJ mol}^{-1}$  for the amine and the radical species, between 20 and 30  $\text{kJ mol}^{-1}$  for the concerted transition geometry, and 40–60  $\text{kJ mol}^{-1}$  for the ylide.

Using COSMO to calculate the electrostatic effect on the molecular energy, the energy of solvation of the isolated species is 1  $\text{kJ mol}^{-1}$  for the methyl radical, 65  $\text{kJ mol}^{-1}$  for the amine radical, 56  $\text{kJ mol}^{-1}$  for the concerted transition geometry, 42  $\text{kJ mol}^{-1}$  for the amine, and 113  $\text{kJ mol}^{-1}$  for the ylide. Comparing these numbers to the supermolecule energies above, we can see that the elec-

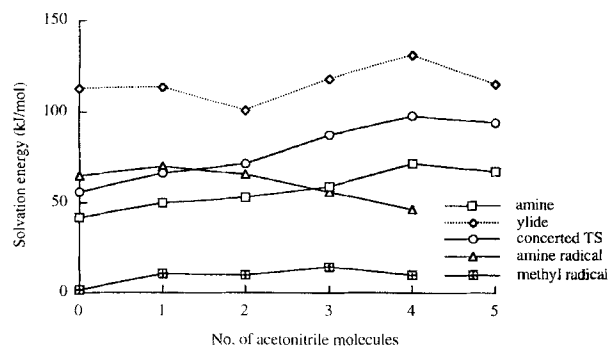


**FIGURE 2.** (a) Optimized COSMO PM3 geometry for amine with five coordinating acetonitrile molecules. (b) Optimized COSMO PM3 geometry for ylide with five coordinating acetonitrile molecules. (c) Optimized COSMO PM3 geometry for concerted transition geometry with five coordinating acetonitrile molecules. (d) Optimized COSMO PM3 geometry for amine radical with four coordinating acetonitrile molecules. (e) Optimized COSMO PM3 geometry for methyl radical with four coordinating acetonitrile molecules.

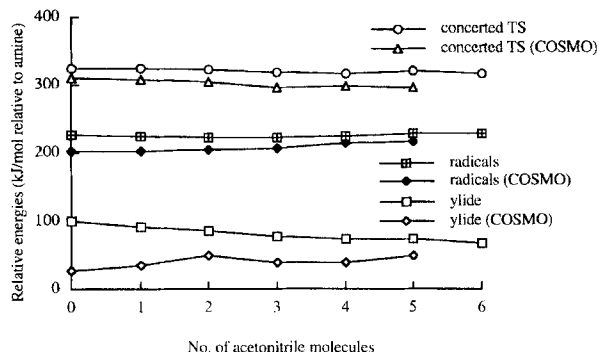


**FIGURE 3.** Energy of complexation of species by number of acetonitrile molecules.

trostatic effects are, in general, larger than specific solute-solvent effects; however, they are of the same order of magnitude, hence, specific effects are of some importance. The effect of acetonitrile molecules inside the cavity on solvation is presented in Figure 4. There is little effect on the energy of the methyl radical, as could be expected. The solvation energy of the amine radical decreases with coordinating acetonitrile molecules, the solvation energy of the amine and concerted transition geometry is increased and then plateaus out, and the ylide solvation energy seems to increase and decrease with number of acetonitrile molecules. It can be seen from this graph that there is a definite change in solvation energy by incorporating solvent molecules in the cavity, and that it may require several coordinating solvent molecules to get an idea of the specific solvent-solute interactions.



**FIGURE 4.** COSMO solvation energy as a function of number of solvent molecules.



**FIGURE 5.** Relative energies of all species with varying number of acetonitrile molecules.

### RELATIVE ENERGIES

The relative energies for the rearrangement are presented in Table II, and graphically as a function of the number of acetonitrile molecules in Figure 5. COSMO is shown to have a similar effect on relative energies as the SCRF MP2/6-31G(d) method of solvation previously reported<sup>17</sup>; the energies of all species are lowered; however, COSMO lowers the relative energy of the amine considerably more than SCRF.

For the supermolecule calculations, it is difficult to assign an appropriate energy for the radical pair pathway, as there are two species involved in the transition structure. The energies reported in this article are the lowest obtained from all possible combinations of the two radicals and the appropriate number of solvent molecules (for six acetonitriles, this corresponds to three solvent molecules on each radical species). From the relative energies of the largest supermolecule calculations presented in Table II, it can be seen that there is some difference between the supermolecule calculations and the single-molecule calculations, both in the "gas phase" and with COSMO. The overall effect of all methods for incorporating solvation effects is that the radical pair rearrangement is favored over the concerted pathway, the supermolecule methods lowering the difference between the two pathways slightly, but not enough for the concerted pathway to be considered the rearrangement mechanism.

Figure 5 shows the behavior of the two supermolecule methods as a function of number of solvent molecules. It is satisfying to note that, for the radical pair and for the ylide, the two methods are converging—indicating that adding the continuum to a supermolecule calculation brings the



energy toward that which an infinite number of solvent molecules would achieve. Energies for the concerted transition geometry are not necessarily converging, and this may be because of the different geometries seen between the gas-phase complex and COSMO geometry.

## Conclusions

We have used the supermolecule approach and a polarizable continuum method in concert to obtain a solvation energy, which takes into account both specific solvent-solute effects and the electrostatic contribution to solvation. The changes in relative energy due to the electrostatic contribution to solvation become rather small after between four and six solvent molecules have been incorporated in the wave function, which puts the calculations comfortably in reach using semiempirical methods. The COSMO method is shown to be a reliable and useful tool in calculating solvation energies as the molecular geometry of the supermolecule can be optimized for a large system in the presence of an reaction field.

From these calculations, the solvent effect on the Stevens rearrangement of methyllummonium formylmethylide has been calculated. There are specific solvent-solute interactions in evidence; two solvent molecules coordinate to the delocalized orbital on the ylide, and remain coordinated in the transition geometry. Energetically, however, it has been determined that there is no effect on the pathway of the reaction, which proceeds via a radical pair mechanism. It is planned to apply this method to rearrangements and reactions which are in competition with the Stevens rearrangement.

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## Supplementary Material

Absolute molecular energies (in eV) for all optimized structures and positions of the acetonitrile molecules in the supermolecules are available upon request from the authors or via the Internet (see footnote \* on page 1444).

## References

1. W. C. Still and F. Guarnieri, *J. Comput. Chem.*, **15**, 1302 (1994).
2. A. Warshel, *Computer Modelling of Chemical Reactions in Enzymes and Solutions*, John Wiley & Sons, New York, 1991.
3. S. Miertus, E. Scrocco, and J. Tomasi, *Chem. Phys.*, **55**, 117 (1981).
4. J. L. Rivail, B. Terry, and M. F. Ruiz-Lopez, *J. Mol. Struct. (Theochem)*, **120**, 387 (1985).
5. A. Klamt and G. Schuurmann, *J. Chem. Soc. Perkin Trans.*, **2**, 799-805 (1993).
6. N. A. Burton, D. V. S. Green, I. H. Hillier, P. J. Taylor, M. A. Vincent, and S. Woodcock, *J. Chem. Soc. Perkin Trans.*, **2**, 331-335 (1993).
7. F. E. Romesberg and D. B. Collum, *J. Am. Chem. Soc.*, **116**, 9187-9197 (1994).
8. D. E. Woon and T. H. Dunning, *J. Am. Chem. Soc.*, **117**, 1090-1097 (1995).
9. K. Morokuma and C. Muguruma, *J. Am. Chem. Soc.*, **116**, 10316-10317 (1994).
10. M. Szafran, M. M. Karelson, A. R. Katritzky, J. Koput, and M. C. Zerner, *J. Comput. Chem.*, **14**, 371-377 (1993).
11. M. Karelson and M. C. Zerner, *J. Am. Chem. Soc.*, **112**, 9405 (1990).
12. T. Furuki, M. Sakurai, and Y. Inoue, *J. Comput. Chem.*, **16**, 378-384 (1995).
13. J. J. P. Stewart, *J. Comput. Chem.*, **10**, 209 (1989).
14. G. L. Heard, K. E. Frankcombe, and B. F. Yates, *Austral. J. Chem.*, **46**, 1375-1388 (1993).
15. G. L. Heard and B. F. Yates, *J. Mol. Struct. (Theochem)*, **310**, 197-204 (1994).
16. G. L. Heard and B. F. Yates, *Austral. J. Chem.*, **47**, 1685-1694 (1994).
17. G. L. Heard and B. F. Yates, *Austral. J. Chem.*, **48**, 1413-1423 (1995).
18. J. J. P. Stewart, MOPAC 93, Fujitsu L. (1993).
19. J. Baker, *J. Comput. Chem.*, **7**, 385 (1986).